The Excited States of Atoms

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MANY of us who count ourselves still young remember the definition in our text books of chemistry, "Atoms are the indivisible constituents of matter." It is said that a young student, who had boldly suggested a possible subdivision of atoms to explain some phenomenon and was sharply reminded by Lord Kelvin that the very word atom is the Greek for indivisible, replied, "There you see the disadvantage of knowing Greek."

We now know that every atom is a complex structure, consisting of a positive electrical charge of known amount and a definite number of negatively charged electrons arranged around the positive charge, and probably moving in orbits like planets around a sun.

Another old and rather deeply rooted idea is that an atom is an entity, possessing always the same definite specific properties. This concept, like that of the indivisible atom, has had to be discarded. We now know that every atom is capable of existing in an infinitely infinite variety of states which may differ markedly in chemical and physical properties.

A well established method of investigating any object is to stir it up and then see what happens. In dealing with atoms, which cannot be seen, this is the only available method of examination. All our knowledge about atoms has come through the finding of a consistent line of interpretation of what happens when matter (a complex structure of atoms) is disturbed in various ways. Only a few of the simpler and more striking effects of such disturbance can be discussed in this brief space.

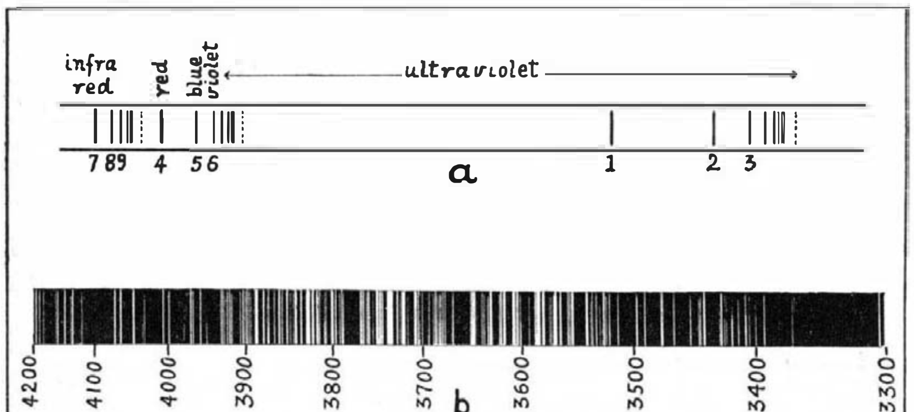


FIGURE 1

ABOVE: *(a). Diagram of spectrum of hydrogen showing series of lines 1, 2, 3, et cetera, in ultraviolet, series 4, 5, 6, et cetera, in the visible and near ultraviolet, and series 7, 8, 9, et cetera, in infra-red. The distances from the left are proportional to light vibration frequencies. Figure 1 (b). Portion of the spectrum of iron. The numbers are wavelengths in units of 0.00000001 centimeter. The extreme left end of the spectrum lies in the violet end of visible region*

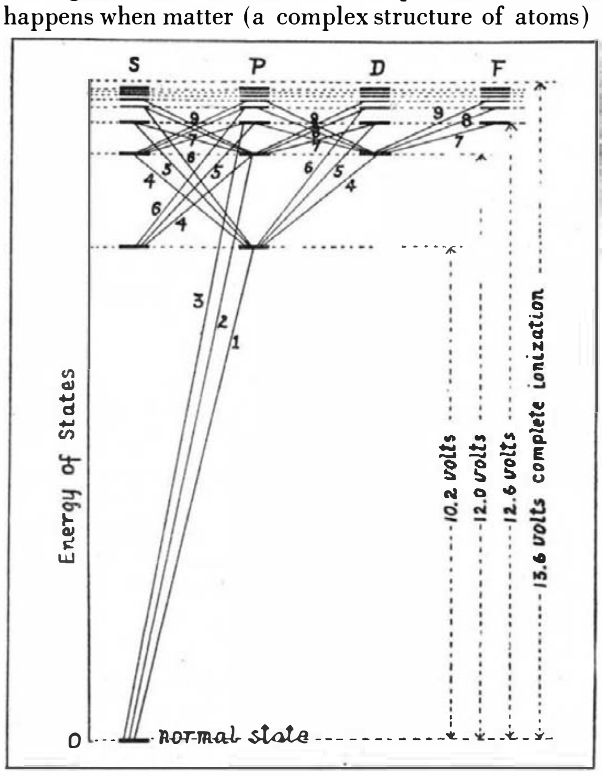


FIGURE 2

Grotrian diagram of the energy states of hydrogen

Most fruitful of all methods of studying atoms has been the examination of the light which they emit under various stimuli, together with the converse study of the kinds of light which they can absorb under various conditions.

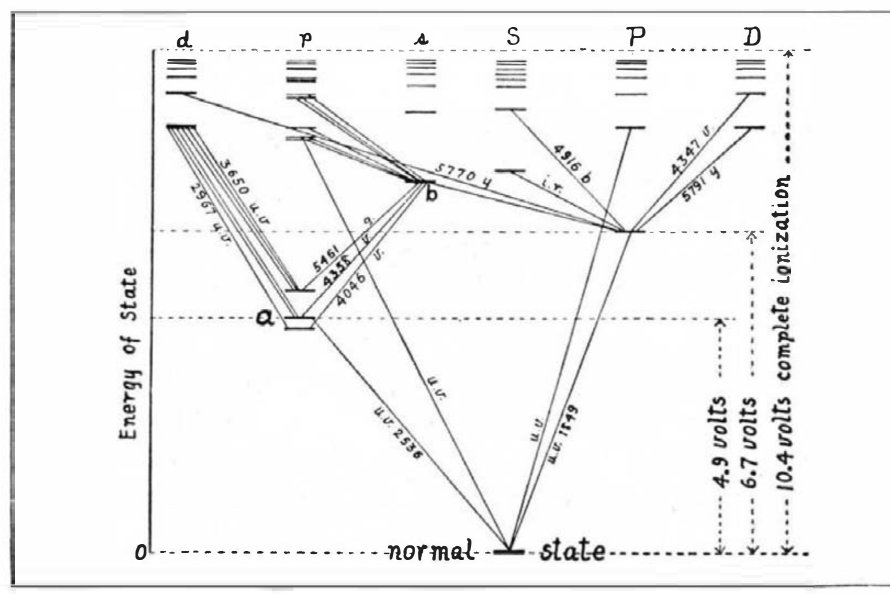
Light passing through a slit may be brought to a focus by a lens, so as to cast an image of the slit on a screen. If a transparent prism is interposed, the light rays are bent, different colors or wavelengths of light being bent differently, so that there are as many separate images of the slit cast on the screen as there are different colors of light in the source. If all wavelengths are present, as in light from an incandescent solid, these images merge into one another, side by side, and the result is the familiar continuous or rainbow spectrum. But if the source of light is a luminous gas, then only light of certain definite wavelengths is found to be present and there is a corresponding set of images of the slit, each in its own color and in a position on the screen which depends upon its wavelength. This set of colored images is the "spectrum" of the gas. If the screen is a photographic plate, the arrangement described above is a spectrograph—capable of giving a permanent photographic record of the spectrum.

The spectrum of a gas is an extraordinarily definite thing, absolutely characteristic of each particular gas. Some spectra are very simple; others are very complicated. Figure 1 (a) shows the simplest spectrum, that of hydrogen, and shows that the spectrum which the eye can see is only a small part of the entire spectrum which can be investigated photographically, or by other methods. Figure 1 (b) shows a small section of one of the most complex spectra, that of iron vapor.

The remarkable definiteness of the spectrum of each kind of atom at once suggests something very definite in the structure or behavior of the atom. These "somethings" are the "states" of the atom, and experiments of the sort to be described later show that light is emitted or absorbed by the atom only as it changes its internal structure from some one of these states to another. This can be illustrated by the so-called "Grotrian" diagram of hydrogen, Figure 2.

FIGURE 3

BELOW: *Grotrian diagram of energy states of mercury. Diagonal lines show transitions between states which produce prominent lines in mercury spectrum. Letters y, g, b, et cetera, indicate color; numbers indicate wavelengths*



The heavy horizontal dashes represent the possible states of a hydrogen atom and the vertical position, or level, is proportional to the energy contained by the atom in these states. The state of least energy, which we can take as the zero energy state, is the "normal" state of the atom, that is, the state in which all hydrogen atoms are found unless some source of energy is acting to increase their energy to that of the other states, which are called the "excited" states. The differences between these states are known to be due to differences in the arrangement of the electrons which exist outside the nucleus, probably in the shape and size of their elliptical orbits. In a hydrogen atom there is only one electron, so that each of these states corresponds to some one of the possible orbits of this electron. In the normal state this orbit is very small, the electron remaining always close to the nucleus (about one hundred-millionth of a centimeter from it).

The states of larger energy correspond to larger orbits, and the increased energy is due to the work done in pulling the electron to a greater distance from the attracting nucleus. The dotted line at the top is the state in which the orbit is so large that the electron flies away and is lost to the atom. The most striking feature of the atom is the existence of these discrete states or orbits, instead of all varieties of orbits as are possible in gravitational motions.

Every change of an atom from a state of higher to a state of lower energy is accompanied by the emission of light whose vibration frequency (the reciprocal of the wavelength) is directly proportional to the difference in energy of the two states. Thus, if W_2 and W_1 are the energies of the two states, the change from state 2 to state 1 gives rise to the emission of light of frequency ν given by $W_2 - W_1 = h\nu$ where h is known as Planck's constant. Thus we see that in changing its state, an atom radiates in the form of light the energy which it loses in the change. If it changes from a low to a higher energy state, the corresponding amount of light energy of the right frequency must be absorbed from the agency which causes the change.

With this explanation, it may be seen to be pos

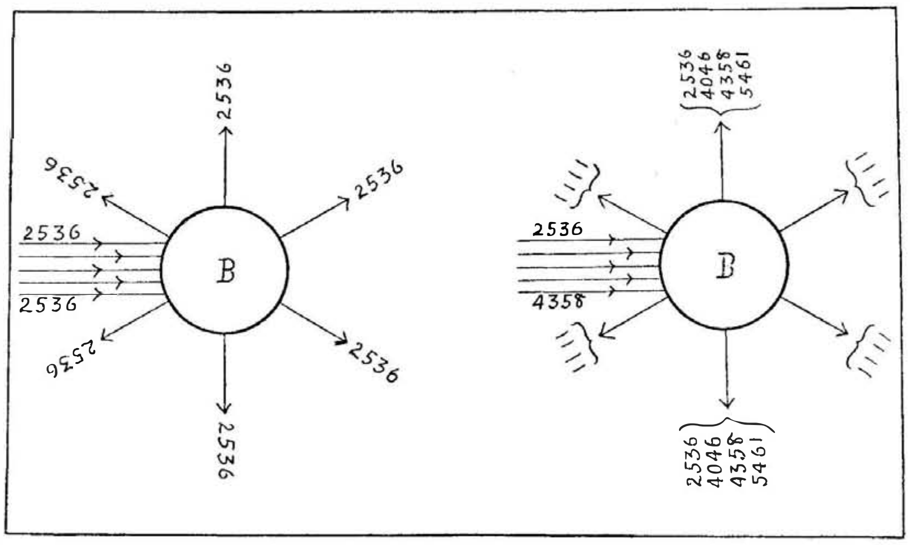


FIGURE 4

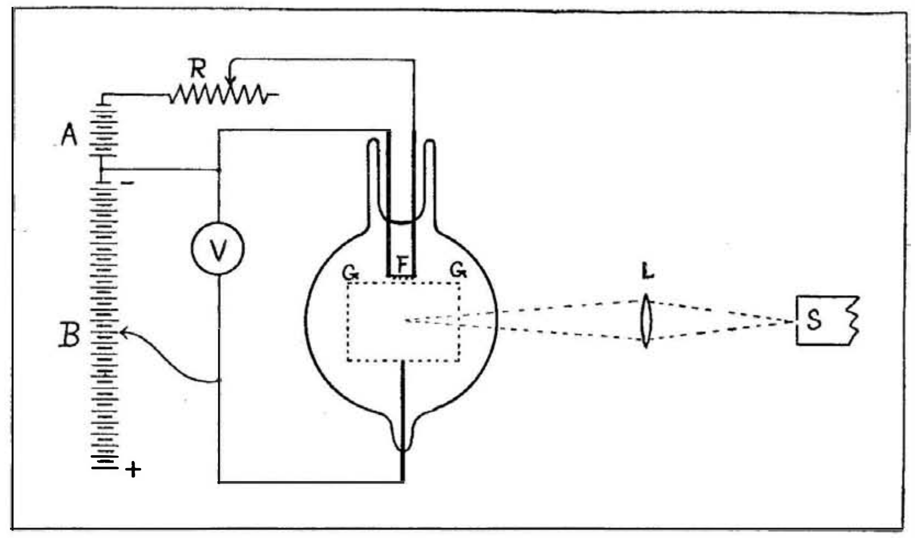


FIGURE 5

sible to unravel a complicated spectrum so as to find out just what energy states must be assumed to exist in the atom in order to account for the observed spectrum. For instance, the spectral lines marked 1, 2, 3, 4—in Figure 1 (a) are due to transitions between energy states as indicated by the correspondingly numbered diagonal lines in Figure 2. The notation S, P, D, F, et cetera, has a significance which is most simply stated by saying that, usually, only those changes of state occur which are between adjacent columns, that is, from S to P, D to P, P to D, et cetera, but not S to F, et cetera.

Figure 3 shows a portion of the similar Grotrian diagram of the states of mercury, with a few of the changes of state which produce the prominent lines in the mercury arc spectrum designated by y, g, b, u.v., and so on, according to the color or ultraviolet character of the light emitted in the change. The numbers correspond to wavelengths of the light in units of one hundred-millionth of a centimeter.

Atoms Absorb and Reradiate Light

We now pass to another phase of investigation by which the validity of this energy state explanation of spectra has been placed on a direct experimental basis. From among numerous types of experiment, two of the simplest and most significant are the following:

(1) *Optical Excitation.* (Figure 4.) Ordinary mercury vapor, for example, can only absorb light of wavelengths corresponding to transitions from the normal state, as shown by the various spectral lines in the series 1, 2, 3, et cetera, and 4, 5, 6, et cetera, in Figure 3. To all other light the normal vapor is transparent. Suppose that a bulb containing mercury vapor is placed in a beam of ultraviolet 2536 light (that is, light having a wavelength of 2536 ten-millionths of a millimeter or Angström units), coming from any convenient source such as a nearby mercury arc. Some of the mercury atoms, in absorbing this light, are "excited" to the state *a*, whence they sooner or later revert to the normal state and re-emit the 2536 light. Thus the mercury vapor absorbs 2536 light and reradiates it in all directions. This reradiated light, called "resonance radiation," has been extensively investigated by R. W. Wood.

If mercury vapor is illuminated by violet light 4358 nothing happens, since the mercury atoms in the normal state cannot absorb it. But if illuminated *simultaneously* by 4358 and 2536, then there is emitted by the vapor light of the four wavelengths 5461, 4358, 4046 and 2536 as a result of the following process: first, mercury atoms are excited to state *a* by absorbing 2536 light; second, these atoms now in state *a* are able to absorb 4358 light and some of them will do so, yielding excited atoms of state *b*. From states *a* and *b*, there are possible the transitions to lower energy states which emit the four spectral lines mentioned above. In a similar way the various energy states may be optically excited, one by one, and the Grotrian diagram verified step by step.

(2) *Excitation by Electron Impact.* Another way of supplying energy in definite amounts to atoms is to bombard them by electrons whose kinetic energy is controlled in the following manner:

In a glass or quartz bulb a filament F is heated to incandescence by current from a battery A, and in this condition it emits electrons which are drawn to a perforated gauze G by applying between F and G a voltage V from a battery B. Many electrons pass through the openings in the gauze and collide with atoms of gas. If the voltage V is large enough, this bombardment suffices to change the atoms from their normal to their various excited states; and in returning to their normal states they emit a spectrum, which serves to identify the states to which they have been changed by the bombardment. This spectrum is examined by concentrating the light which is produced on the slit of a spectrograph, by means of a lens L.

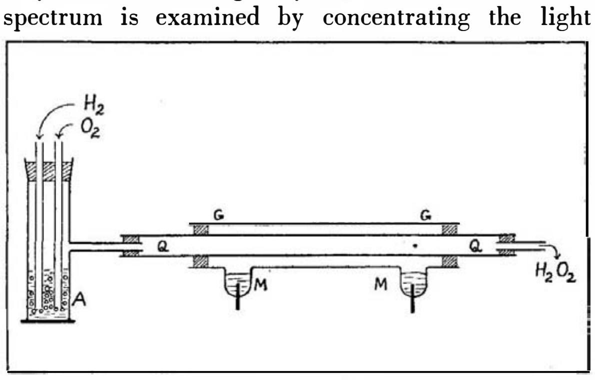


FIGURE 6

The experimental procedure is to increase the bombarding voltage V in small steps, and examine the spectrum at each step. In case the bulb contains mercury vapor, for example, no light at all is produced by the bombardment if V is less than 4.9 volts. At this voltage the line 2536 appears in the spectrum, but no other line appears (except faintly, due to complicating phenomena) until the voltage is increased to 6.7 volts, at which the line 1849 appears. Similarly the other lines appear one by one as the voltage is raised until, at 10.4 volts, the entire arc spectrum is present.

Now the kinetic energy of an electron which has moved through 4.9 volts, is easily calculated, and when this is divided by Planck's constant h we have exactly the frequency corresponding to 2536 light. Similar calculations give the other lines of the mercury spectrum, and some of these are indicated to the right in Figure 3. Thus we have made a direct measure of the energies of the various states of mercury and verified the energy state diagram which was suggested to interpret the spectrum. Similar studies of other gases and vapors have been made.

A series of brilliant investigations, principally by Franck and his pupils in Göttingen, has disclosed the fact that the energy stored up in excited atoms may be used in other ways than to produce light, and this discovery will doubtless have wide applications in chemistry and in the art of illumination. A single illustration, taken from work done in Princeton by Professor Taylor and his collaborators, will serve to suggest the possibilities of this discovery in chemistry.

It is well known that hydrogen, H_2, and oxygen, O_2, when mixed, do not combine unless ignited, and then they combine with explosive violence to form water, H_2O. But they may be otherwise united through the agency of excited atoms as follows:

In Figure 6, QQ is a quartz tube. A glass tube GG is provided with mercury electrodes MM and evacuated. Oxygen and hydrogen gases are made to stream through the quartz tube and a mercury arc is maintained in the surrounding tube. Although the oxygen and hydrogen in the quartz tube are intensely illuminated by light from the mercury arc, they are unaffected thereby since they are transparent to those wavelengths of light supplied by the mercury arc, and thus absorb no energy from it.

What Is Photocatalysis?

If, however, the oxygen and hydrogen are bubbled through mercury, as at A, so that they carry along with them a little mercury vapor into the quartz tube, the gases emerge combined in the form of hydrogen peroxide, H_2O_2. The action is this: the mercury atoms within the quartz tube absorb the 2536 light from the mercury arc and are changed to the excited state *a*, Figure 3. If a mercury atom while in this excited state collides with a hydrogen molecule, its energy may be transferred to the molecule and is sufficient to split this molecule into two separate atoms. In this atomic state the hydrogen atoms are able spontaneously to start the reaction which leads to the production of hydrogen peroxide. The mercury vapor emerges from the reaction unchanged.

This "photocatalytic" action is typical of many others, such as that of chlorophyll in leaves to render sunlight effective for plant growth, and that of "sensitizers" in photographic work. The discovery of the reason for these catalytic actions will doubtless expedite their applications to many useful purposes.

It is realized that so brief a survey as this cannot be complete. It is hoped only that it may serve to disclose one direction of recent research in this important branch of atomic physics and to suggest the point of view, the methods and the possible applications of this work.